Fluoride in Acid Solutions

DOC316.53.01236

Direct Measurement ISE Method **Method 8323**

0.1 to 100.0 mg/L F **ISE Electrode**

Scope and Application: For industrial waters (solutions below a pH of 5)

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Meter	Electrode
*sens**ion***™ 4 meters	5192800
*sens**ion***™ 2 meters[1]	5192800

[1] The user must construct the calibration curve with the *sens**ion*** 2 meter.

Before starting the test:

Refer to the meter user manual for meter operation. Refer to electrode manual for electrode maintenance and care.
Prepare the electrode. Refer to *Electrode assembly* and *Condition the electrode* in this procedure.
In solutions below a pH of 5, hydrogen ion complexes some of the fluoride ions, forming HF or HF_2^-, which the electrode will not detect. To free the complexed fluoride, adjust the pH of the solution so it is weakly acidic to weakly basic before analysis.
Do not use a strong base (such as sodium hydroxide) for adjustment since the amount of base added will vary from sample to sample. Using a strong base can also change the ionic strength of the sample and alter measurement accuracy.
Dilution of samples and standards with a large excess of sodium acetate will buffer the pH and help adjust the total ionic strength of samples and standards to the same level.

Collect the following items:

Description	Quantity
Fluoride ISA buffer pillows (TISAB)	1 mL
Sodium acetate, ACS	varies
Fluoride standard solutions:	
10.00-mg/L F or	varies
2.00-mg/L F or	varies
100.0-mg/L F	varies
Potassium Chloride Reference Electrolyte Gel Cartridges	1
Water, deionized	varies

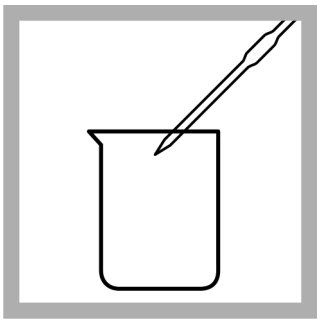
Collect the following items: (continued)

Description	Quantity
Beaker, 50-mL, polypropylene	3
Tensette pipet, 1.0–10.0 mL or	1
25 mL Class A volumetric pipet	1
Class A 1000 mL volumetric	1
Bottle, wash, 500-mL	1
Cylinder, graduated, 25-mL, poly	3
Platinum Series Fluoride Combination Electrode, BNC	1
*sens**ion***™2 Portable pH/ISE Meter.	1
OR	
*sens**ion***™4 Laboratory pH/ISE Meter	1
Stir Bar, 7/8 X 3/16 in. (22.2 x 4.8 cm)	4
Stirrer, electromagnetic with stand and stir bar	1

See *Consumables and replacement items* for reorder information.

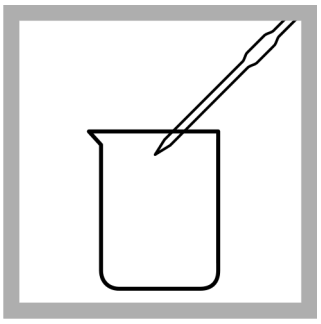
Fluoride in Acid Solutions method

1. Prepare a 15% sodium acetate solution by dissolving 150 g of reagent grade sodium acetate in 1000 mL of deionized water. Prepare enough solution to dilute all the samples and standards.



2. Using deionized water, prepare a background solution containing all the sample matrix components except fluoride. Use this solution to prepare the standards.

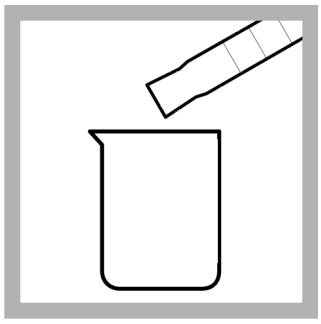
If a standard prepared with background solution gives the same reading (after sodium acetate dilution) as standard prepared with pure sodium acetate, it is not necessary to prepare a background solution.



3. For calibration, prepare fluoride standards by adding fluoride to the background solution.

Prepare fresh standards every two weeks if standards are less than 10 mg/L F^-.

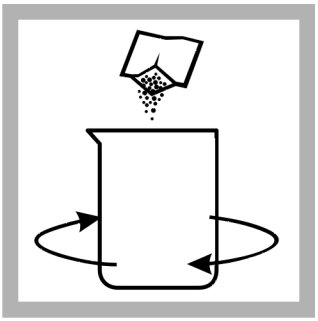
When testing with a direct reading fluoride meter, use two standards. When testing with a pH/mV meter, use three standards.



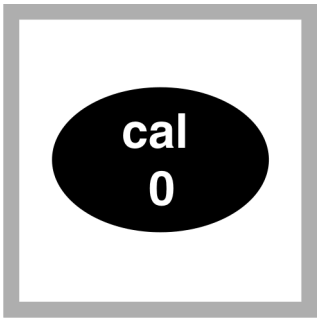
4. Dilute each standard 10:1 with sodium acetate solution (9 parts sodium acetate solution to 1 part standard) to prepare the buffered solution. Mix thoroughly.

For example, measure 3 mL of standard (with background solution) and dilute it with 27 mL of sodium acetate solution.

Fluoride in Acid Solutions method (continued)

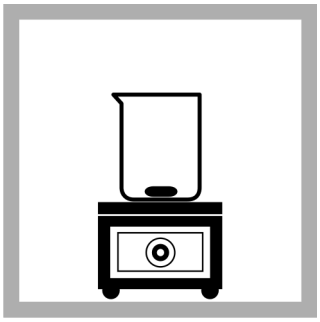


5. Add the contents of one Fluoride Total Ionic Strength Adjustment Buffer (TISAB) Powder Pillow to 25 mL of the prepared buffered sample. Stir to dissolve.



6. Turn the meter on. Set the electrode type to BNC. Set the units to mg/L. Press **CAL**.

Refer to the meter user manual for details.



7. Place the beaker with the 1-mg/L prepared buffered standard on a magnetic stirrer. Stir at a moderate rate.

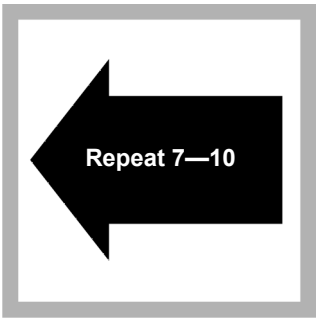
8. Place the electrode into the standard.

9. Edit the display to show the concentration of the standard.

Press **ENTER** and accept the concentration.

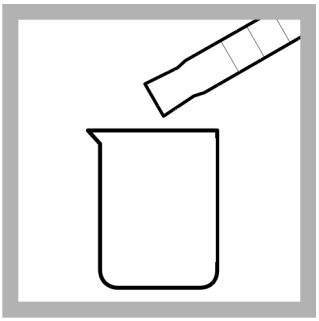
10. The display will show **Stabilizing** until the measurement is complete.

Remove the electrode from the standard solution Rinse with deionized water and blot dry.



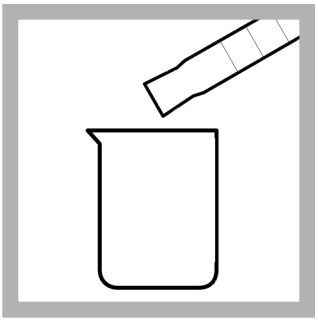
11. Repeat steps 7–10 for the 10-mg/L and 100 mg/L standards.

After the last standard is measured, store the calibration in the meter. Refer to the meter user manual for details.

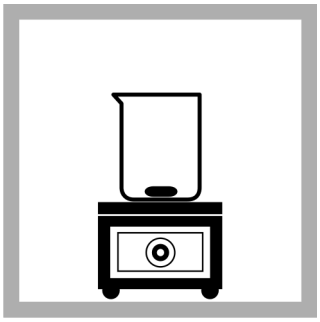


12. Measure the sample into 50-mL beakers to measure 25 mL of prepared buffered sample.

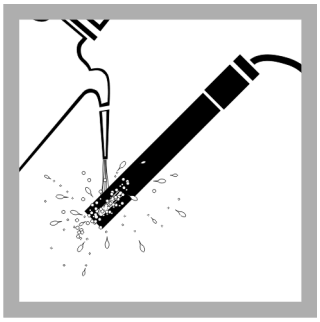
For example, measure 3 mL of sample and dilute it with 27 mL of sodium acetate solution. Pour 25 mL of this solution into a 50-mL beaker.



13. Dilute each unknown 10:1 with sodium acetate solution before measurement.



14. Place a stir bar in the beaker and set the beaker on a magnetic stirrer. Stir at a moderate speed.



15. Rinse the electrode with deionized water and blot dry.

16. Place the electrode into the sample. When the reading is stable, record the value.

Electrode assembly

1. Remove the cap from the electrolyte cartridge.
2. Visually inspect the Luer tip of the electrolyte cartridge. If air is present, rotate the feed-screw counter-clockwise until gel expels the air and fills the tip.
3. Fit the cartridge outlet tube firmly onto the inlet tube of the electrode body (Figure 1).

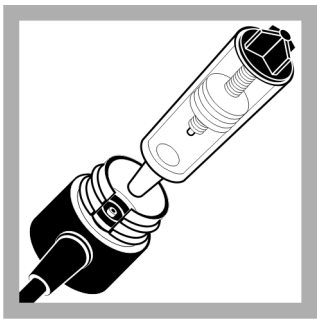


Figure 1 Attach the outlet tube

4. Place the dispenser unit over the electrolyte cartridge. Screw the dispenser unit onto the electrode body until reaching the stop. Do not over tighten.
5. Dispense the electrolyte gel by pressing the pump button. Repeat this procedure until gel is visible at the reference outlet (Figure 2).

Figure 2 Dispense the electrolyte gel

6. Rinse the electrode with deionized water. Do not scratch the crystal.
7. To remove an empty cartridge, unscrew the dispenser unit and rotate the cartridge counterclockwise while gently pulling it out of the electrode.

8. Connect the BNC connector of the electrode to the BNC connector on the meter (Figure 3).

Figure 3 BNC connector

Note: *One BNC and one 5-pin connector are on the back of the meter. Choose the BNC for the fluoride electrode. Disconnect the pH electrode from the 5-pin connector when using the BNC connector.*

Condition the electrode

Condition and store the electrode in 1 mg/L Fluoride standard storage with Ionic Strength Adjuster for 15 to 30 minutes.

For electrode storage procedures, refer to the Fluoride Electrode Instruction Manual.

Clean the Lanthanum Fluoride Crystal

It may be necessary to clean the LaF crystal on the sensing tip of the probe if it becomes covered with organic film or buildup.

1. Put a small amount of fluoride toothpaste on a soft toothbrush or cloth.
2. Gently rub the LaF crystal with the toothpaste using a circular motion. Rub until the film is removed.
3. Thoroughly rinse the probe with deionized water and blot dry. Verify the crystal is clean. If not, repeat cleaning and rinsing until it is clean.
4. If the crystal becomes contaminated by oil, grease, or fingerprints, soak for a few minutes in isopropyl alcohol then rinse with deionized water.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Cations	Do not interfere
Cl^-, Br^-, SO_4^{2-}, HCO_3^-, PO_4^{3-}, acetate	Do not interfere
OH^- (Hydroxyl ions)	Interferes: refer to *pH Effects*. Some ions, such as CO_3^{2-} or PO_4^{3-}, make the sample more basic, which increases OH^- interference, but do not directly interfere with the electrode operation.
CO_3^{2-} or PO_4^{3-}	Can make the sample more basic and increase OH^-

pH Effects

In solutions with a pH below 5, hydrogen ion complexes some of the fluoride ions, forming the undissociated acid HF and the ion HF_2^-. Figure 4 shows the proportion of free fluoride ion in acid solutions.

If the background ionic strength is high and constant in comparison with the ion being measured, the activity coefficient is constant and activity is directly proportional to ion concentration. Total ionic strength adjustor is added to standards and samples to make the background ionic strength high, decomplex fluoride, and adjust the solution pH to 5.0–5.5.

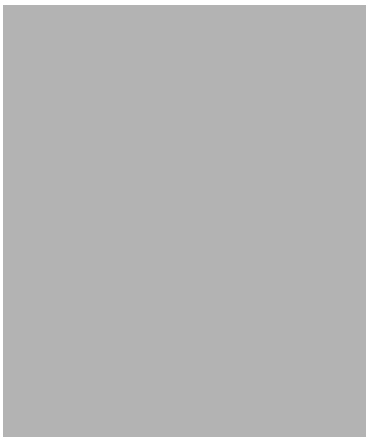


Figure 4 Ratio of free F^- in acid solutions

Sample collection, preservation and storage

- Collect samples in plastic bottles.
- Samples may be stored up to 28 days.

Accuracy check

Standard additions method (sample spike)
To verify measurement accuracy, perform a standard addition spike on the sample. The spike should roughly double the measured concentration without significantly diluting the sample.

To perform a standard addition sample:

1. Use the *Spike volumes* table to determine the concentration and volume of standard to spike the sample. The volume of sample transferred must be accurate.
2. Add the amount and concentration specified in the *Spike volumes* table to the sample.
3. After adding the standard, proceed with the calculations. Results from 90-110% recovery are considered acceptable. Calculate percent recovery as follows:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:
X_s = measured value for spiked sample in mg/L

X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L

K = known value of the spike in the sample in mg/L

Calculations

1. $X_u = \frac{X_i \text{ ì } V_u}{V_u + V}$

Where:

X_i = measured value of unspiked sample in mg/L

V_u = volume of separate unspiked portion in mL

V = volume of spike in mL

2. $K = \frac{C \times V}{V_u + V}$

Where:

C = concentration of standard used in spike in mg/L

V = volume of spike in mL

V_u = volume of separate portion before spike in mL

3. Final calculation plugging in Xu and K: $\%\ \text{Recovery} = \frac{100(X_s - X_u)}{K}$

Example:

A sample was analyzed and read 5.0 mg/L F^-. As directed in the *Spike volumes* table, a 1.0-mL spike of 100-mg/L F^- standard was added to another 25-mL sample, giving a final standard addition result of 8.75 mg/L.

Calculate the percent recovery as follows:

1. $X_u = \frac{5.0\ \text{mg/L} \times 25\ \text{mL}}{25\ \text{mL} + 1\ \text{mL}} = 4.81\ \text{mg/L}$

2. $K = \frac{100\ \text{mg/L} \times 1\ \text{mL}}{25\ \text{mL} + 1\ \text{mL}} = 3.85\ \text{mg/L}$

3. $\%R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.81)}{3.85} = 102.3\ \%\ \text{Recovery}$

Table 3 Spike volumes

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.1–0.6	25	100	0.1
0.6–1.0	25	100	0.2
1.0–1.5	25	100	0.3
1.5–3.0	25	100	0.5
3–6	25	100	1.0
6–10	25	100	2.0
10–15	25	100	3.0
15–25	25	1000	0.5
25–35	25	1000	0.7
35–50	25	1000	1.0
50–100	25	1000	2.0

Summary of method

The fluoride electrode consists of a sensing Lanthanum Fluoride element bonded into an epoxy body. When the sensing element contacts fluoride ions in a solution, a potential develops across the sensing element. The potential is proportional to the level of fluoride ions present. The potential is measured against a constant reference potential with a pH/mV meter or ISE meter.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Fluoride Standard Solutions:			
1.00-mg/L F or	varies	500 mL	29149
10.00-mg/L F or	varies	500 mL	40520
100.0-mg/L F	varies	500 mL	35949
Potassium Chloride Reference Electrolyte			
Gel Cartridges	varies	2/pkg	2546902
Sodium Acetate, ACS	varies	454 g	17801H
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Beaker, 50-mL, polypropylene	3	each	108041
Bottle, wash, 500-mL	1	each	62011
Cylinder, graduated, 25-mL, poly	3	each	108140
Fluoride Combination Electrode, BNC, w/ filling solution	1	each	5192800
*sens**ion*** 2 Portable pH/ISE Meter	1	each	5172500
OR			
*sens**ion*** 4 Laboratory pH/ISE Meter	1	each	5177500
Stir Bar, 7/8 x 3/16 in. (22.2 x 4.8 cm)	4	each	4531500
Select one based on available voltage:			
Stirrer, electromagnetic, 115 VAC, with stand and stir bar	1	each	4530001
Stirrer, electromagnetic, 230 VAC, with stand and stir bar	1	each	4530002
Tensette pipet 1.0–10.0 mL	1	each	1970010
Class A, 25 mL volumetric pipet	1	each	1451540
Safety bulb pipet filler	1	each	1418900
Class A, 1000 mL volumetric flask	1	each	1457453

Optional apparatus

Description	Unit	Catalog number
Electrode Washer	each	2704700
Pipet, TenSette, 0.1 to 1. 0 mL	each	1970001
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	2185696

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Updated March 2011, Edition 5